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2012 International Symposium on Safety Science and Technology Study on clean coal technology with oil agglomeration in Fujian Province

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Abstract

Based on the Fujian coal resource utilization and distribution, samples from Peifeng coal mining were chosen as research object. This paper studies the effects of deashing with oil agglomeration technology, which mainly includes of agglomeration size, coal concentration, oil types and its dosage, alcohol types and dosage, PAM types and dosage. The results showed that the ash content can be reduced from 32% to 2.8% by one time and the ash rejection rate is arrived to 93.0% when the slurry concentration is 11.1% and oil dosage is 12.5%.

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Keywords: clean coal technology; oil agglomeration; deashing

1. Introduction

With the fast development and expansion of industry, conventional non-renewable energy resources are facing with a severe crisis. Nowadays global energy security has become a more popular topic, since petroleum which is known as the "blood of industry" and "economy of the black gold" will be dried up within this century. How to make more effective use and protection of the only resources available on earth will be the question which needs to be discussed on the global table. However, during the 80s and 90s, the clean coal technology (CCT) began to rise and is now growing into matured. This promising technology as well as the research of coal substitution for petroleum product will take the main role to alleviate the energy crisis. Including the United States, Japan and European Union, many other countries have put great efforts in the development and practical application of clean coal products in earlier research, and succeed. In 1995 China launched the research on clean coal technology, and is still under relatively immature stage[1-3]. China is in possession of rich coal resources, the use of coal resources accounted for 75% in energy consumption every year on an average. Under the dual pressure of energy security and environmental pollution, clean coal technology will be the future of China's energy industry[4].

The energy situation focusing on shortage of oil and gas, abundant energy resources import, and limited low-ash and low-sulfur coal reserves is very discordant to Fujian construction and development needs[5]. In the research, Fujian high-ash coal's special quality featuring higher metamorphic grade, stronger hydrophobicity and better lipophilicity makes us aware of its very significant potential. Effective use of these resources will help to relieve the energy security situation in Fujian province. The product of oil agglomeration will be used for the production of ultra-low-ash coal-water slurry, which can replace kerosene and diesel oil burned in a combustion boiler[6], thus to effectively reduce the dependence on

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petroleum products, relieve the situation of petroleum products supply shortage, and reduce the environmental pollution caused by coal. Safeguard of Fujian energy security has important economic significance and social benefits.

This study started with analysis on lowering the ash content in the Fujian high-ash coal, and oil agglomeration technology with two different types of selective oil (two kinds of petroleum products and four kinds of vegetable oil) was used as the major method to reduce the impurities contained in coal samples from YongDing city. Oil works as liquid bridge between coal particles. Hydrophilicity and lipophilicity differences between coal and impurities were the basis during deashing process. Experiments on oil agglomeration tests with different particle sizes of coal samples give the basic data we needed to confirm that oil agglomeration worked well for Fujian high-ash coal deashing. Thus it founded a solid foundation for our further studies. And some other experiments are designed and carried out to identify the oil consumption, and the effect of solid concentration, the surfactants and other factors.

2. Experimental materials and methods

2.1. Main raw materials and equipment

Proximate analyses of coal sample is shown in table 1. Bridging liquid: diesel, kerosene, soybean oil, rapeseed oil, peanut oil, tea oil. Agents: dodecanol, DL-2-Octanol. Equipment is shown in table 2.

Table 1. Proximate analyses of coal sample

Sample	Aad(%)	Mad(%)	Vad(%)	FC(%)
PeiFeng	32.1	4.08	6.07	57.75

Table 2. Experimental equipment

Device	Model	Manufacturer
Sampling prototype	CGJ100-3	Cheng Gong mining equipment manufacturing, Xiamen city
Precision electric stirrer	JJ-1	Guohua Changzhou
Muffle furnace	SX2-8-10	Chenggong mining equipment manufacturing, Xiamen city
Electronic balance	BSA2243	Sartorius scientific instruments (Beijing)
Constant temperature water bath kettle	PKSR4	Shanghai Jinghong experimental equipment

2.2. Experiments method

The coal is crushed and grinded in a prototype system to <1 mm. A conical flask containing 50g fine coal sample and proper amount water and oil is placed under an agitator. The coal-water-oil mixture is stirred at a speed of 2400 r/min for 5-10min, until the mass of particle is visible and the impurities are separated from coal sample. After filtrating, washing, drying the product, the low-ash clean coal is obtained. With ligroin extracting the oil in the reunion, take 1g samples for ash determination. The experimental process is shown in Fig. 1.

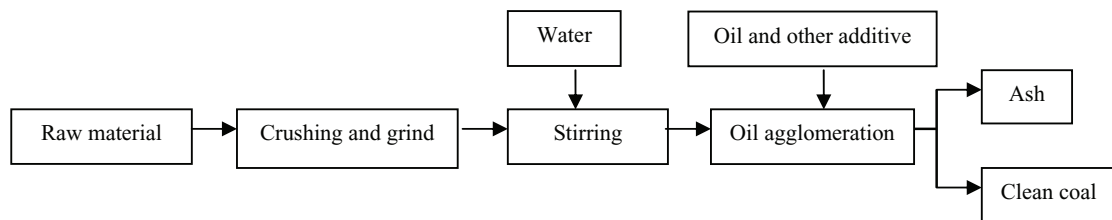


Fig. 1. Experimental process.

2.3. Analysis of experiment results

Based on the ash determination data and by contrasting the differences, we are able to ultimately determine the best conditions for coal deashing experiment. Test method for ash content determination is GBT 212–2002. The results is calculated by the following equation

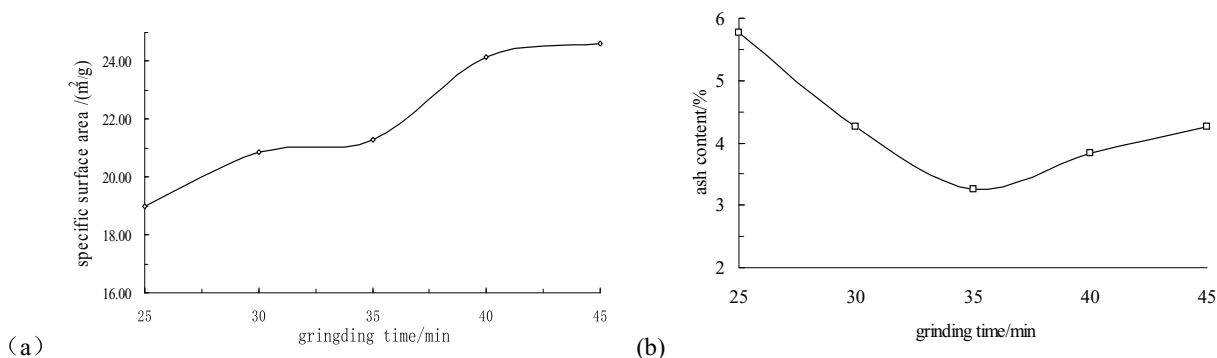
$$A_f = G_1 / G_2 \times 100\% \quad (1)$$

where A_f is indicates ash content, %; G_1 is indicates the constant weight of the residues after burning, g; G_2 is indicates the weight of raw coal, g.

3. Results and discussion

3.1. Effect of fineness

The particle size has a direct impact on ash removal effect in agglomeration process[7]. Smaller particle diameter is in favor of coal deashing and impurity dissociation, but it also means greater energy input. The decrease of the particle size greatly increases the specific surface area of coal with the same mass, and at the same time, it makes it easier for particles to follow the water flow and movement, thus it contributes to increasing contact opportunities of coal particles and the bridging liquid, and makes the process more easily accomplished. By controlling the grinding time we can change the coal particle size. The specific surface area is shown in Fig.2 and the change of ash content is shown in Fig. 3.



Solid concentration is 12.5%, oil consumption is 16%, agitating time at speed of 2400r/min is 10 minutes

Fig. 2. Illustration of (a) specific surface area changed with the grinding time and (b) the effect of the grinding time on agglomeration.

In Fig. 2, it shows that with the prolonging of grinding time, particle surface area is evidently increased, that means the particle size is also decreased along with the prolonging of time. However, at 40 minutes or later, the particle size is basically unchanged, the specific surface area is maintained in 24 m²/g. At this point, the dispersion degree of ore particles reaches the maximum, the diameter is the minimum, and surface energy the maximum.

If table footnotes should be used, place footnotes to tables below the table body and indicate them with superscript lowercase letters. Be sparing in the use of tables and ensure that the data presented in tables do not duplicate results described elsewhere in the article.

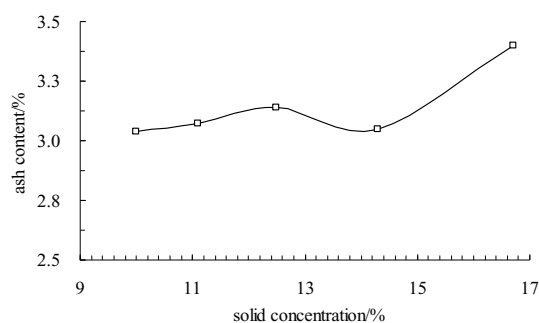
Fig. 3 gives a message that with the decrease of particle size, ash content of product first decreased and then slightly increased. When grinding time reaches 35 minutes, ash content of product is the minimum. Specific surface continues to increase, and oil agglomeration effect is enervated. The reason is that the minification of coal particle size helps the enveloped impurities better separated[8], thereby improving the deashing effects. When grinding time is 35min, ash content is reduced to 3.25%, in this case, impurity particles and coal particles separation is near complete. Over 40 minutes, ash content has a certain rise. It's because with the prolonging of grinding time, the effects of particle size on coal and impurity separation can be hardly changed, but to reduce the coal fineness, surface energy will keep increasing, viscosity is enhanced, fine particles of impurities are easy to be entrained when aggregating, in addition, high temperature and long-time grinding can result in surface being oxidized[9-11], enhancing its hydrophilicity, which leads to the increase of ash content. In order

to further experiment and compare, and to obtain better deashed product, experiments thereafter will use coal samples grinded for 40 minutes.

3.2. Effect of solid concentration

The solid concentration directly affects the collision probability of coal particles and emulsion droplets, and is associated with agglomerating rate. It is an important factor that affects the experiment result[12].

It can be seen from Fig. 4 that for the high-ash Peifeng coal with the rise of solid concentration, the overall level of the ash content tends to rise as well. When the solid concentration is 16.7%, the ash content is highest value: 3.4%. The reason is that for high-ash coal, increasing solid concentration is actually also increasing impurity concentration. Under the effect of high shear force field, the impurity particles move with water and collide coal particles and oil droplets. Fine coal particles and impurity particles come closed to each other and in some particular position the surface effect is more obvious, therefore the possibility of impurity particles being wrapped in the process will increase. Meanwhile, reducing water consumption, means that the oil droplet concentration will increase, too. At the end, oil selectivity is relatively weakened, it may also lead to part of the ash being wrapped by fine coal particles during the reunion process.



Grinding time is 40 minutes, oil consumption is 16%, agitating time at speed of 2400r/min is 10 minutes

Fig. 4. Effect of the slurry concentration on agglomeration.

It can be seen from Fig. 4 that for the high-ash Peifeng coal with the rise of solid concentration, the overall level of the ash content tends to rise as well. When the solid concentration is 16.7%, the ash content is highest value: 3.4%. The reason is that for high-ash coal, increasing solid concentration is actually also increasing impurity concentration. Under the effect of high shear force field, the impurity particles move with water and collide coal particles and oil droplets. Fine coal particles and impurity particles come closed to each other and in some particular position the surface effect is more obvious, therefore the possibility of impurity particles being wrapped in the process will increase. Meanwhile, reducing water consumption means that the oil droplet concentration will increase, too. At the end, oil selectivity is relatively weakened, it may also lead to part of the ash being wrapped by fine coal particles during the reunion process.

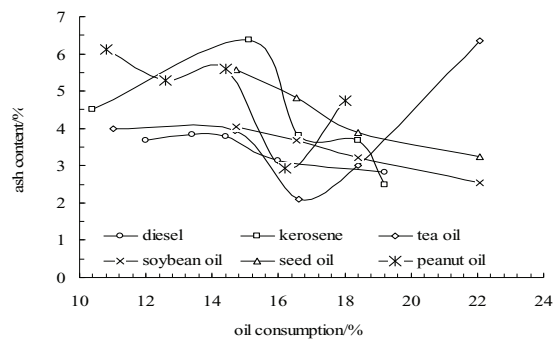
3.3. Effect of oil consumption and oil type

Different amount of oil decides the concentration of bridging liquid droplets. Different kinds of oil show different affinity and capacity to coal sample[13-14], both of which play a key role in oil agglomeration.

Fig. 5 suggests that oil consumption adjusting often lead to large fluctuations of ash content. Effect of oil type varies in two trends: for diesel, soybean oil, rapeseed oil with increase of amount, the effect of the ash removal is enhanced and among them, the curve of diesel is the lowest. For kerosene, peanut oil and tea oil, there are leaps and bounds in Fig. 5. For example, with 15.1% kerosene the curve reaches the highest ash value : 6.37% ,for peanut oil with 14.4% dosage the figure is 5.59%, but generally they are in the downward trend within the experiment limits. When tea oil consumption is 16.6%, the ash content come to a minimum of 2.11% it suggests that the dosage amount of tea oil should be within 17%. Reasonable explanation for these phenomena will be: 1. In the test, emulsifier is not considered, and the stirring speed of the stirrer is limited, so oil droplets in water will easily absorb each other while in movement. It makes oil in the water distributed unequally. Large droplets form a thick oil layer on the surface of coal particles and the selectivity is declined, and become

easier to envelop impurities. On contrary, the layer of small droplets formed is thinner, the formation of the hydrophobic layer is also pretty stable, so impurities are tend to be rejected. But during the experiment, the absorption between oil droplets happens at random, thus making the measured data fluctuating. 2. The iodine value of the aliphatic hydrocarbons is relatively smaller (less than 20) and physical adsorption plays the main role in agglomeration, experimental effect depends on the amount of oil. However, vegetable oil contains a large number of unsaturated bonds (Table 3[16]), and the iodine value is averagely above 90. In addition to physical adsorption, chemical adsorption is playing a more important role (mainly in the form of ionic bonds with stronger bond energy) [15], so its property is more reactive, and the experimental effect displays sensitivity for the amount of oil while the dependence is weaker. 3. The diversity of compositions and the differences of average single molecule cross-sectional area among the oils generate the influences on experimental result. For the oil whose components with strong selectivity content is higher, its collecting performance is poorer[16], so better ash rejection is shown more obviously when the dosage is higher. And for the oil whose components with strong selectivity content is lower, its collecting performance is more effective, better ash rejection is more likely to appear when the dosage is lower. Besides, the single molecule cross-sectional area (Table 4) of every component directly add an extra effect on particle absorption.

In summary, the effect of vegetable oil is the sum of many factors, the situation is very complex, and the further experiments are needed. On the other hand, the effect of aliphatic hydrocarbon in the experiment features a positive correlation with the dosage.



Solid concentration is 12.5%, Grinding time is 40 minutes, agitating time at speed of 2400r/min is 10 minutes

Fig. 5. Effect of the oil concentration on agglomeration.

Table 3. Composition of different vegetable oils

Vegetable oil	18: 1 (oleic acid%)	18: 2 (linoleic acid%)	18: 3 (linolenic acid%)	stearic acid%	else%
Soybean oil	10-12	22-25	50-55	7-9	3-4
Seed oil	2-5	10-35	10-20	5-15	1-2
Peanut oil	11.7	43.2	36.5	-	3.5
Tea oil	1.8	80.5	8.66	-	9.04

Table 4. Single molecule cross-sectional area

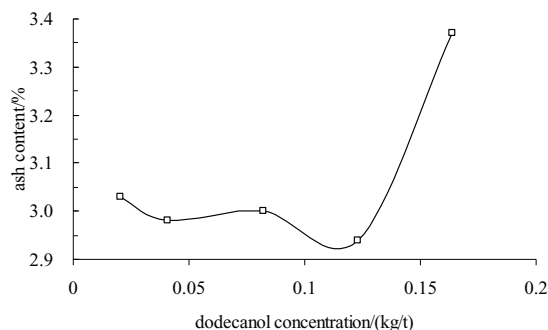
Organic acid	Single-molecule cross-sectional area/nm ²	Organic acid	Single-molecule cross-sectional area/nm ²
Stearic acid	0.244	Linolenic acid	0.682
Oleic acid	0.566	Isolinolenic acid	0.600
Vaccenic acid	0.485	Castor oil acid,	1.094
Linoleic acid	0.595	Isoricinoleic acid	0.797
Isolinolic acid	0.533		

selectivity strength of higher fatty acids: stearic acid> palmitic acid> soft oleic acid> oleic acid> linolenic acid.

Rank of collecting performance strength of higher fatty acids: linolenic acid> oleic acid> soft oleic acid> palmitic acid> stearic acid.

3.4. Effect of dodecanol

In the agglomerating process, the selection and use of auxiliary agents may have a negative or positive effect on the final statistic[17]. We found that the Peifeng coal samples tend to have a sensitive react to surfactants (mainly long-chain alcohols) and flocculant (various types of polyacrylamide). The effect is illustrated by experiments on anionic PAM and dodecanol, and the result is shown in Fig. 6.



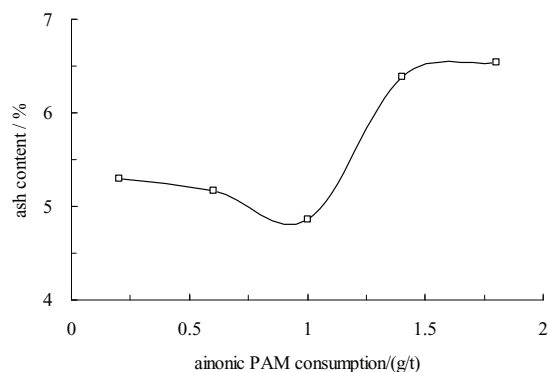
Solid concentration is 14.3wt%, grinding time is 40 minutes, diesel consumption is 16% agitating time at speed of 2400r/min is 10 minutes

Fig. 6. Effect of the dodecanol concentration on agglomeration.

In Fig. 6, the ash content was first reduced with the increase of the amount of dodecanol. When the dosage of dodecanol was 0.123kg/t, ash content came to 2.94% which was the lowest point; However, when the amount of dodecanol increased over 0.13kg / t, the ash content spurted, until it reached the top at an ash content of 3.37% with the dodecanol amount of 0.164kg / t. The phenomenon can be explained as follow: Dodecanol is easily dispersed under the vigorous shear force field, and aligned on the oil droplet surface, forming a stable hydration film on it, so as to maintain the shape of oil droplets in water and make it difficult to be annexed, thereby increasing the collision probability of oil droplets and coal particles. But when dodecanol on the oil droplet surface was overloaded, oil droplets would turn to be more hydrophilic and more non-selective. Therefore, in the further studies, pharmaceutical amount should be controlled within a small range.

3.5. Effect of PAM

The 1wt.%polyacrylamide solution used in the experiment was prepared in the water bath under constant temperature of 60 °C beforehand. By controlling the volum of solution added into the slurry, we obtained the curve (shown in Fig. 7) that tells the relevance between ash content and PAM amount.



Solid concentration is 14.3wt%, dodecanol consumption is 0.123kg/t, grinding time is 40 minutes, diesel consumption is 16% agitating time at speed of 2400r/min is 10 minutes

Fig. 7. Effect of the PAM concentration on agglomeration.

In Fig.7 it is clearly shown that ash content went up with the increase of anionic PAM, and then tended to be static, when it was at 6.4% -6.5% with the largest amount of consumption. The reason was that anionic PAM hydrolysed and ionized in water, making electrostatic effect with strong bond energy ($> 48\text{kJ}$) which is almost irreversible the main role in mineral adsorption. However, this kind of absorption relying on electrostatic double-layer effect has poor selectivity, clay mineral is often adsorbed too[18]. Moreover, PAM is a kind of macromolecular compounds, it can link coal particles together into unconsolidated floc, but due to the poor dispersion in water, the floc often traps the impurity particles, and this trend is aggravated with the increase of anionic PAM as well as weakening of its selectivity, leading to the rise of ash content.

4. Conclusions

The following conclusions can be drawn by the experiments on oil agglomeration of the Peifeng coal samples:

- (1) Oil agglomeration worked well for Peifeng coal deashing;
- (2) When diesel consumption is 12.5wt.%, without using other additives under high concentration slurry, ash content was reduced to about 2.8%, ash rejection is as high as 93% in a single test;
- (3) high-ash coal is suitable for ash reduction under high concentration slurry.

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